High activity catalysts for the total oxidation of naphthalene based on mesoporous CeO_2 modified with low levels of copper

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Abstract

Cu-CeO_2 catalysts with low Cu-loadings present high catalytic activity and also clean combustion, as only CO_2 was detected as a reaction product, for the total oxidation of naphthalene (Np). The improved behaviour has been related to the presence of one specific O-species, which corresponds to defective oxides or to surface oxygen ions with low coordination.

1. Introduction

An important family of VOCs is the Polycyclic Aromatic Hydrocarbons (PAHs) [1]. Naphthalene is usually considered as a model PAH compound, since it is one of the most abundant PAH in flue gases, the simplest and the least toxic of them. Among the non-noble metal catalysts reported for the total oxidation of Np, CeO_2 is one of the most (if not the most) efficient catalysts. In order to increase the activity of CeO_2 catalysts different preparation methods, in order to modify the crystallite size, the specific surface area or the number of oxygen vacancies, have been reported [2]. In the present work we have explored the modification of the mesoporous CeO_2 characteristics by adding a small amount of copper (chemical element with redox and basic properties) and its effect on catalytic behaviour has been evaluated.

2. Experimental

Mesoporous cerium oxide and copper doped cerium oxide have been prepared using poliethylene glycol. The heat tretament was in air at 600ºC. The reaction feed consisted in all cases of ca. 450 vppm naphthalene in a mixture of 20 vol.% oxygen and 80 vol.% helium. A total flow rate of 50 ml•min^{-1} was used and the catalysts occupied a constant volume, giving a GHSV of ca. 75000 h^{-1} for all the catalysts. The catalysts synthesized have been characterized by several techniques: N_2-adsorption, XRD, Raman spectroscopy, XPS, and FT-IR spectroscopy.

3. Results and discussion

Figure 1 shows the T50 values (reaction temperatures for a yield to CO_2 of 50%) for pure CeO_2, pure CuO and Cu-doped CeO_2 catalysts. As can be seen the mixed Cu-CeO_2 with low Cu contents (Cu/Ce at. ratio between 0.0025 and 0.02) present the lowest T50 and consequently the highest activity. An excess of copper leads to a decrease in the catalytic activity. Additionally, in brackets it is shown the selectivity to CO_2 (at 20% conversion). Pure CuO, pure CeO_2 and the Cu-CeO_2 catalyst with a Cu/Ce ratio of 0.2 apart from CO_2 yielded other by-products, such as phenanthrene, naphthalene dione, dimethyl phthalate, benzene, alkyl benzenes, benzaldehyde, toluene and xylenes, some of which are highly toxic. Conversely, Cu-doped CeO_2 catalysts with Cu/Ce at. ratios from 0.25 to 5% were totally selective to CO_2.

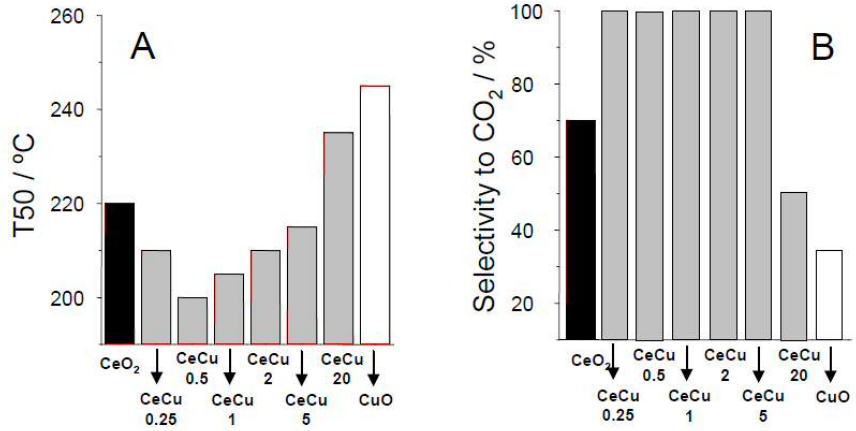

Figure 1. Influence of the Cu/Ce at. ratio on the T50 (A) and on the selectivity to CO_2 (B) during the naphthalene oxidation. Note: CeCu*x* corresponds to a Cu/Ce at. ratio of *x*/100.

Copper used in this synthesis has been incorporated into the CeO_2 lattice, as confirmed by the decrease of the CeO_2 lattice parameter, producing a higher density of oxygen defect sites. Related to this, the proportion of one specific O-species which corresponds to defect oxides or to surface oxygen ions with low coordination has increased. These surface oxygen defects are very reactive and can easily activate the reactants, in this case naphthalene and oxygen, increasing the activity and also the selectivity to carbon dioxide.

4. References

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